THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part III. Discussion of the Infra-red Data

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1. Introduction

Comparatively few investigations on the infra-red spectra of the hydroxides appear to have been made and even these mainly concern themselves with the $3\,\mu$ region. In the present part we shall discuss the data available for LiOH, $LiOH \cdot H_2O$, NaOH, $Ca(OH)_2$ and $Mg(OH)_2$. Duval and Lecomte (1941) had reported the infra-red spectra of LiOH, $Ca(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$ for the region $600-1600$ cm.$^{-1}$ which falls outside the range of even the first order combinations of most of the lattice frequencies of these substances. In many of the cases studied by them there appear strong maxima in the region of 880 cm.$^{-1}$ and 1440 cm.$^{-1}$ corresponding to the strong absorption maxima usually observed with the carbonates. In view of the meagreness of the data for the lattice frequencies active in the infra-red and also since it appears to us that the substances used by Duval and Lecomte in their study have been contaminated by the atmospheric carbon dioxide to form the carbonates, we do not propose to discuss their data.

2. The Infra-red Spectra of LiOH, $LiOH \cdot H_2O$ and NaOH

(i) *LiOH and* $LiOH \cdot H_2O$.—The infra-red absorption spectra of LiOH and $LiOH \cdot H_2O$ have been recorded by Jones (1954) in the $3\,\mu$ region using thin films of the substances, the frequencies of the absorption maxima of the OH vibrations being respectively 3678 and 3574 cm.$^{-1}$ The internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion in these two cases belong respectively to the classes A_{2u} of D_{4h} and B_u of C_{2h} and are in each case the only infra-red active internal mode theoretically possible and hence the respective maxima at 3678 and 3574 cm.$^{-1}$ are to be identified with them. That the infra-red frequencies in these cases are only slightly different from the Raman active frequencies is indicative of weak coupling between the hydroxyls. The diminution of the hydroxyl frequency in $LiOH \cdot H_2O$ by about 100 cm.$^{-1}$ is hence largely to be attributed

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to the proximity of the water molecules to the hydroxyls. Two other maxima at 3000 cm.$^{-1}$ and 1586 cm.$^{-1}$ respectively due to the stretching and bending vibrations of the water molecules in $LiOH \cdot H_2O$ have also been reported by him, the diminution in their frequencies being due to causes already discussed.

An absorption maximum at 7195 cm.$^{-1}$ has also been observed by Jones in LiOH and identified as the overtone of 3678 cm.$^{-1}$ According to theory this overtone is forbidden in the infra-red and only the combination between the Raman active (3664 cm.$^{-1}$) and the infra-red active (3678 cm.$^{-1}$) vibrations is allowed in the infra-red. Anharmonicity can be expected to be the cause of the violation of the selection rules. The large difference (161 cm.$^{-1}$) between the anticipated value for the overtone and the observed value indicates the presence of considerable mechanical anharmonicity. However, further studies are required to elucidate this feature more fully.

(ii) *Sodium hydroxide.*—The infra-red absorption spectrum of NaOH in the form of thin films has been studied by Busing (1955) and a sharp maximum at 3637 cm.$^{-1}$ is reported by him. This is to be identified with the theoretically expected infra-red active internal vibration of the hydroxyls antisymmetrically with respect to the centre of inversion and belonging to the class B_{1u} of D_{2h}. The small difference of 5 cm.$^{-1}$ between the Raman active and infra-red active hydroxyl frequencies indicates that the coupling between the hydroxyls is very weak.

3. THE INFRA-RED SPECTRA OF Ca(OH)$_2$ AND Mg(OH)$_2$

Unlike the above cases, the infra-red spectra of Ca(OH)$_2$ and Mg(OH)$_2$ exhibit complex structures in the $3\,\mu$ region and it was therefore suspected that the actual unit cell of the structure should be larger than that derived from X-ray studies (Mara and Sutherland, 1953). However, reinvestigations of the structures by both X-ray and neutron diffraction methods have only revealed the correctness of the structure proposed earlier. So far, only tentative explanations have been offered for the complex features of the spectra.

It has already been shown in Table IV of Part II that in the cases of Ca(OH)$_2$ and Mg(OH)$_2$, there are possible four infra-red active fundamentals of which one is due to the internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion and three others are due to translatory and rotatory oscillations. Besides these, the selection rules for combinations and overtones indicate that the combinations between the Raman active fundamentals and the infra-red active fundamentals (*viz.*, $A_{1g} \times A_{2u}$;

$A_{1g} \times E_u$; $E_g \times A_{2u}$; $E_g \times E_u$) are allowed in the infra-red. The first overtones and first order combinations of the infra-red active frequencies between themselves and similarly the combinations and overtones of the Raman active frequencies are forbidden in infra-red absorption. An absorption maximum can be identified as a combination of the differential type only if the corresponding summational is also observed. The complex features exhibited by the spectra of $Ca(OH)_2$ and $Mg(OH)_2$ are explicable on the basis of these criteria.

(i) *Calcium hydroxide.*—The infra-red absorption spectrum of $Ca(OH)_2$ has been reported by Busing and Morgan (1957). Table I shows the frequencies of the absorption maxima and the nature of their origin. The

TABLE I

Absorption maxima in Ca(OH)₂ and their interpretation

Absorption maximum in cm.⁻¹	Their suggested origin	Calculated value in cm.⁻¹
4164	3616+282+263	4161
3932	3644+282; 3616+322	3926; 3938
3899	3644+247	3891
3877	3616+263	3879
3720	3616+98	3714
3644	A_{2u}	..
3629*	?	..
3523	3616−98	3518
3364	3644−282	3362
3333†	3616−263	3353
3294	3616−322	3294
3073	3616−282−263	3071

* Very weak; † See text for alternative explanation.

prominent maximum at 3644 cm.$^{-1}$ observed by them, when the crystal is orientated such that the incident beam is inclined to the c-axis, represents the hydroxyl stretching vibrations (antisymmetrically with respect to the centre of inversion) under the class A_{2u}. The numerous other maxima are explicable as arising due to (i) the combinations of the frequency 3644 cm.$^{-1}$ with the Raman active lattice frequencies, and (ii) combinations of the Raman active frequency 3616 cm.$^{-1}$ with the infra-red active lattice frequencies. The actual interpretation of the facts was arrived at by considering the combinations of the former type first and then by choosing from amongst the remaining maxima those pairs of frequencies whose mean value was near 3616 cm.$^{-1}$ By this process it was possible to discover also the three lattice frequencies (98, 263 and 322 cm.$^{-1}$) active in the infra-red. The calculated and observed values shown in Table I are in fair agreement except for the frequency at 3333 cm.$^{-1}$ The only other explanation that could be given for this maximum, without disturbing the consistent scheme of assignments arrived at for the other frequencies, is that it is a combination, forbidden by selection rules, viz., 3616−282; the corresponding summational (3616 + 282) is also observed at 3899 cm.$^{-1}$ The infra-red activities of these are presumably to be attributed to their contiguity to strongly active infra-red frequencies. The appearance of the Raman frequency 282 cm.$^{-1}$ in combinations (differential and summational) with the infra-red active frequency of 3644 cm.$^{-1}$ vindicates our earlier identification of it as a genuine Raman shift of Ca (OH)$_2$.

(ii) *Magnesium hydroxide.*—The infra-red absorption spectrum of Mg (OH)$_2$ has been investigated in detail recently by Mara and Sutherland (1953) and also by Benesi (1959). Using fine powders Benesi has observed a single sharp intense absorption maximum at 3698 ± 2 cm.$^{-1}$ corresponding to the internal vibrations of the hydroxyls (antisymmetrically with respect to the centre of inversion) belonging to the class A_{2u}. Mara and Sutherland who used single crystals of Mg (OH)$_2$ report numerous maxima in addition to a maximum at 2·71 μ (corresponding to 3698 cm.$^{-1}$) which appears when the c-axis of the crystal is inclined to the incident beam. The explanation of the several maxima shown in Table II is rather indirect since neither the Raman active nor the infra-red active lattice frequencies have so far been observed. The numerous maxima arise evidently due to combinations, (i) between the Raman active frequency 3651 and three infra-red active lattice frequencies and (ii) between the infra-red active frequency 3698 cm.$^{-1}$ and the three Raman active lattice frequencies. These combinations should appear on either side of the frequency region 3651–3698, the mean value of the corresponding summational and differential frequencies being centred

TABLE II

Absorption maxima in Mg(OH)$_2$ and their interpretation

Observed maxima		Their suggested origin	Calculated values	
in μ	in cm.$^{-1}$		in cm.$^{-1}$	in μ
2·06	4854	Combinations of higher order	..	..
2·19	4566	do.	..	..
2·24	4464	3698+2×380	4458	2·243
2·32	4310	3651+380+293	4324	2·313
2·45	4082	3698+380	4078	2·452
2·47	4049	3651+390	4041	2·474
2·49	4016	3698+324	4022	2·486
2·53	3953	3651+293	3944	2·535
2·64	3788	3651+127	3778	2·647
2·71	3690	A$_{2u}$	..	..
2·74	3650	A$_{1g}$?	..	..
2·83	3534	3651−127	3524	2·838
2·97	3367	3651−293; 3698−324	3358; 3374	2·978; 2·964
3·01	3322	3698−380	3318	3·014
3·06	3268	3651−390	3261	3·066
3·08	3247*	..	..	..

* See text for explanation.

about either 3651 or 3698 cm.$^{-1}$ The identification of the corresponding summational and differential frequencies is facilitated by the similarity of their behaviour in the spectra obtained for two different orientations of the crystal. For example, the maxima at 2·45 μ and 3·01 μ are observed only when the incident beam is perpendicular to the *c*-axis and not when it is parallel to the *c*-axis.

The wavelengths of the absorption maxima are given by Mara and Sutherland to only two places of decimals and it can be seen that the frequency 3690 observed by them differs (by 8 cm.$^{-1}$) from the more accurate measurement of Benesi. In view of this possibility of errors of the order of 10 cm.$^{-1}$ in the observed values, the agreement between the calculated and observed values of Table II should be considered quite satisfactory. The analysis of data reveals that there should be observed in the case of Mg (OH)$_2$ the following lattice frequencies: (a) 324 and 380 cm.$^{-1}$ in the Raman effect; (b) 127, 293 and 390 cm.$^{-1}$ in the infra-red absorption. The value of the third Raman active lattice frequency might probably be 451 cm.$^{-1}$ as shall be seen below. It is possible to explain the maximum observed at 3247 cm.$^{-1}$ as a differential, i.e., 3698—451, the frequency 451 cm.$^{-1}$ being assumed to be of the Raman active type. In that case, the corresponding summational also should be observed at 4149 cm.$^{-1}$, i.e., at 2·41 μ. But, such a maximum has not been observed, probably because of its falling close to the strong absorption at 2·45 μ and being obscured by it. However, the above is only a tentative explanation. It is rather surprising that there should be observed at 3650 cm.$^{-1}$ in the infra-red, a frequency closely agreeing with the Raman active frequency, in violation of the rule of mutual exclusion.

The crystal structure of Mg (OH)$_2$ is a more closely packed one than that of Ca (OH)$_2$ as is evident from a comparison of their lattice constants, which are given by:

(i) Mg (OH)$_2$: $a = 3·12$; $c = 4·73$ A.U.

(ii) Ca (OH)$_2$: $a = 3·59$; $c = 4·91$ A.U.

Consequently, the interionic forces in Mg (OH)$_2$ would be stronger than in Ca (OH)$_2$ and the fact that the lattice frequencies of Mg (OH)$_2$ are higher than those of Ca (OH)$_2$ is therefore not surprising. The lower atomic mass of Mg would also be responsible for higher frequencies, in the case of modes involving movements of the magnesiums.

It is interesting to note that in all the cases discussed herein, the infra-red active hydroxyl frequencies are always higher than the Raman active hydroxyl frequencies. In the latter case, the dipole moments produced at the two hydroxyls related by the centre of inversion are opposite to each other resulting in their cancellation and hence the vibration is infra-red inactive. On the other hand, in the case of the infra-red active vibrations, the dipole moments produced at the two hydroxyls are additive. Because of the fact that there is a displacement of charge, or in other words, a polarization of the medium taking place in the case of the infra-red active vibration, the potential energy and hence the restoring force for this mode is

greater than in the case of the Raman active mode. The higher value of the infra-red active hydroxyl frequency is hence intelligible.

In conclusion, the author wishes to express his deep sense of indebtedness to Professor Sir C. V. Raman, F.R.S., N.L., for the encouragement and valuable suggestions that he gave during the course of this investigation.

4. SUMMARY

In each of the cases of LiOH, LiOH·H$_2$O, NaOH, Ca(OH)$_2$ and Mg(OH)$_2$ the stretching vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion give rise in infra-red absorption to a single sharp intense maximum at about 3650 cm.$^{-1}$ as is to be theoretically expected. In all cases, the infra-red active hydroxyl frequency is found to be higher than the corresponding Raman active mode and the origin of this feature is explained.

The spectrum of Ca(OH)$_2$ recorded with single crystals exhibits on either side of the principal maximum due to the hydroxyl vibration, numerous other maxima which have hitherto remained unexplained. Some of them arise due to combinations between the observed Raman active lattice frequencies and the infra-red active hydroxyl frequency. The rest are explicable as combinations between the Raman active hydroxyl frequency and infra-red active lattice frequencies. Features similar to those observed in the spectrum of Ca(OH)$_2$ are exhibited by Mg(OH)$_2$ also, and have been explained in an analogous fashion. No experimental data regarding the infra-red active lattice frequencies of Ca(OH)$_2$ and the Raman active and infra-red active lattice frequencies of Mg(OH)$_2$ are available. The values of these are also revealed by the above analysis.

5. REFERENCES

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